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Lithium-7 NMR Studies of $\text{Li}_{1-x}\text{CoO}_2$ Battery Cathodes

by

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LITHIUM-7 NMR STUDIES OF $\text{Li}_{1-x}\text{CoO}_2$ BATTERY CATHODES

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ABSTRACT

Lithium-deficient cathode materials $\text{Li}_{1-x}\text{CoO}_2$, where $x = 0.1, 0.4$ and 0.6 were prepared electrochemically from the stoichiometric parent compound ($x = 0.0$). The materials were observed to be air-stable, and x-ray diffraction characterization yielded good agreement with the *in situ* studies of Dahn and co-workers, regarding changes in lattice parameters. In addition to both static and magic angle spinning (MAS) ^7Li NMR, measurements, the samples were investigated by EPR and cobalt K-edge NEXAFS. The removal of Li is accompanied by compensating electrons from the Co d-orbitals, as evidenced by both shifts in the NEXAFS peak and the observation of EPR signals due to spins localized on the Co ions. These spins, in turn, result in dramatic ^7Li chemical shifts (89 ppm for $x = 0.6$) and line broadening. Whereas MAS analysis of $\text{Li}_{0.9}\text{CoO}_2$ indicates two magnetically inequivalent Li sites, the spectra become too broad to resolve different sites for higher values of x . Finally NMR linewidth and spin-lattice relaxation measurements as a function of temperature suggest a modest increase in Li^+ ion mobility for Li-deficient samples as compared to the parent compound.

INTRODUCTION

LiCoO_2 is one of the leading cathode materials in secondary lithium batteries, despite the relatively high cost of cobalt. Lithium ions can be electrochemically (and reversibly) deintercalated from the parent compound to form $\text{Li}_{1-x}\text{CoO}_2$, and cell voltages lie in the 3.5 - 4.5 V range as the value of x increases from 0.0.^{1,2} Although there have been extensive electrochemical and structural studies of this cathode material, little is known about the local environment of the Li^+ ions because of their extremely small x-ray scattering power. Neutron diffraction could certainly be of use in this regard although there have been no reports of neutron studies of Li-deficient cathode material. For this reason, ^7Li nuclear magnetic resonance (NMR) studies were undertaken. ^7Li NMR spectra can provide information about the local environment of the Li ion, through a variety of interactions. Among these are the nuclear quadrupole interaction, which is present when the site symmetry is low, and the chemical shift arising from either conduction electrons (Knight shift) or interactions with nearby paramagnetic ions. Both of these effects can lead to shifting and broadening of the resonance.

Supplementary measurements performed on these materials include x-ray diffraction, to verify that expected changes in the unit cell parameters occur as lithium is removed; electron paramagnetic resonance (EPR) to identify the main source of NMR broadening; and near edge x-ray absorption fine structure (NEXAFS), to provide supplementary information about the changes in the cobalt electronic structure which accompany Li-deintercalation.

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EXPERIMENTAL

$\text{Li}_{1-x}\text{CoO}_2$, where $x = 0.1, 0.4$ and 0.6 , was prepared using electrochemical titration of commercial LiCoO_2 (as received, from FMC Corp.). The electrolyte solution was $2.0\text{M LiAsF}_6 + 0.4\text{M LiBF}_4$ in methyl formate. The current density was 0.2 mA/cm^2 . After titration the powder was washed in methyl formate and then dried at room temperature under vacuum for 16 hours. Atomic absorption analyses on Li and Co concentrations revealed Li to Co mole ratios of 0.87, 0.58 and 0.52 for the expected compositions $(1-x)$ of 0.9, 0.6 and 0.4, respectively. All samples were deemed air stable, by checking for reproducibility of selected x-ray, EPR and NMR measurements on samples exposed to ambient atmosphere, compared to samples sealed under argon. X-ray diffraction patterns of the $\text{Li}_{1-x}\text{CoO}_2$ samples were obtained with a Phillips PW1840 powder diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants of the as-received (stoichiometric) LiCoO_2 were $a = 2.823(2)\text{ \AA}$ and $c = 14.066(2)\text{ \AA}$, which are in good agreement with literature values.³

NEXAFS measurements were carried out in transition mode on powdered samples at Beamline X-23B of the National Synchrotron Light Source at Brookhaven National Laboratory. CoO was employed as a reference standard and run concurrently with the lithiated samples in order to obtain improved energy calibration. Two different monochromator slit widths were utilized, 1mm and 2mm, the former giving a resolution of better than $\pm 0.1\text{ eV}$. X-band EPR measurements were performed on powdered samples in quartz EPR tubes, with an IBM/Bruker ER-220D spectrometer, utilizing 100kHz field modulation to record absorption first-derivative spectra. Both magic angle spinning (MAS) and wide line ^7Li NMR spectra of packed powder samples were obtained by Fourier transformation of a single-pulse sequence, with a typical 90° pulse length of $3\text{ }\mu\text{s}$, using a Chemagnetics CMX-300 spectrometer. Spin-lattice relaxation times were measured by saturation recovery. Aqueous LiCl solution was employed as a chemical shift reference.

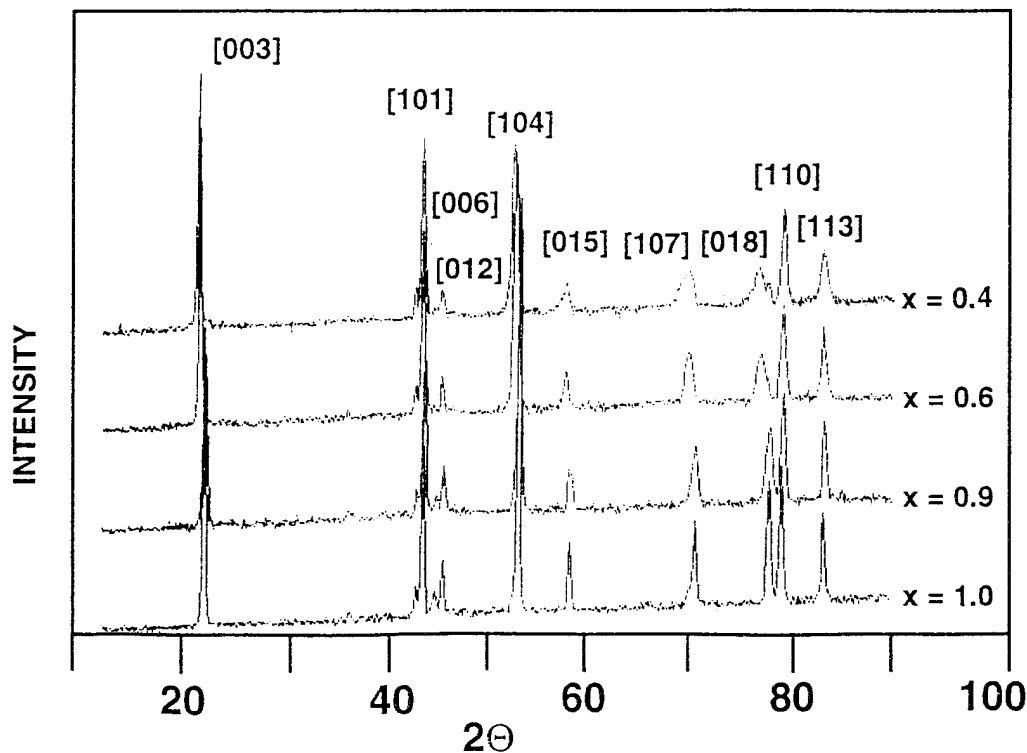


Figure 1a. X-ray diffraction results for Li_xCoO_2 , indicating specific lattice reflections.

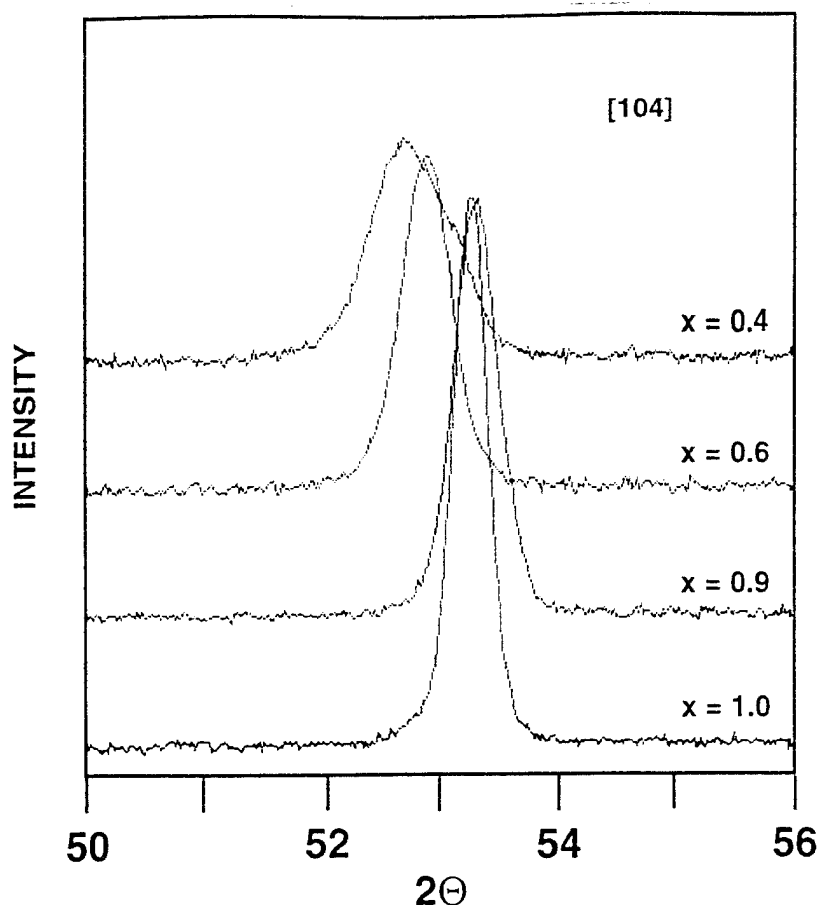


Figure 1b. Expanded scale diffraction, showing [104] reflection of Li_xCoO_2

RESULTS AND DISCUSSION

The x-ray patterns of the Li_{1-x} samples, shown in Fig. 1a, indicate evidence of a small quantity of Co_3O_4 in the initial LiCoO_2 material. The use of internal and external standard methods for measuring phase quantities yield an estimate of approximately 3 wt% of this impurity phase. It has been found by step potentiodynamic cyclic sweeps and overpotential measurements that insertion and de-insertion reactions of $\text{Li}_{1-x}\text{CoO}_2$ proceed as single-phase reversible reactions over at least three phases for $0.0 < x < 0.7$.¹ These phases have been characterized by *in situ* x-ray diffraction studies, which revealed significant expansion of the c-lattice parameter from $0.07 < x < 0.25$, and a lattice distortion from hexagonal to monoclinic symmetry at $x = 0.5$.² Our x-ray results are in agreement with the more detailed *in situ* findings. In particular, shifts to lower Bragg angles for the [003], [104], [107] and [018] reflections are observed as well as splitting of the [018] peak. This agreement is significant in that it validates the use of *ex situ* spectroscopic studies of the ionic and electronic behavior of cathode materials.

The cobalt K-edge x-ray absorption spectrum of the stoichiometric sample is displayed in Fig. 2. The energy range from about 10 eV below the main absorption edge, usually referred to as the "white line", to about 20 eV above the edge is the NEXAFS region, which corresponds to dipole-allowed transitions of 1s-states into unoccupied 4p-states. The range from about 20 eV extending to ~ 1000 eV above the edge is referred to as the extended x-ray absorption fine structure (EXAFS) region, and corresponds to ionization of the core (1s) electrons. The EXAFS spectrum contains information that is often readily converted to nearest-neighbor

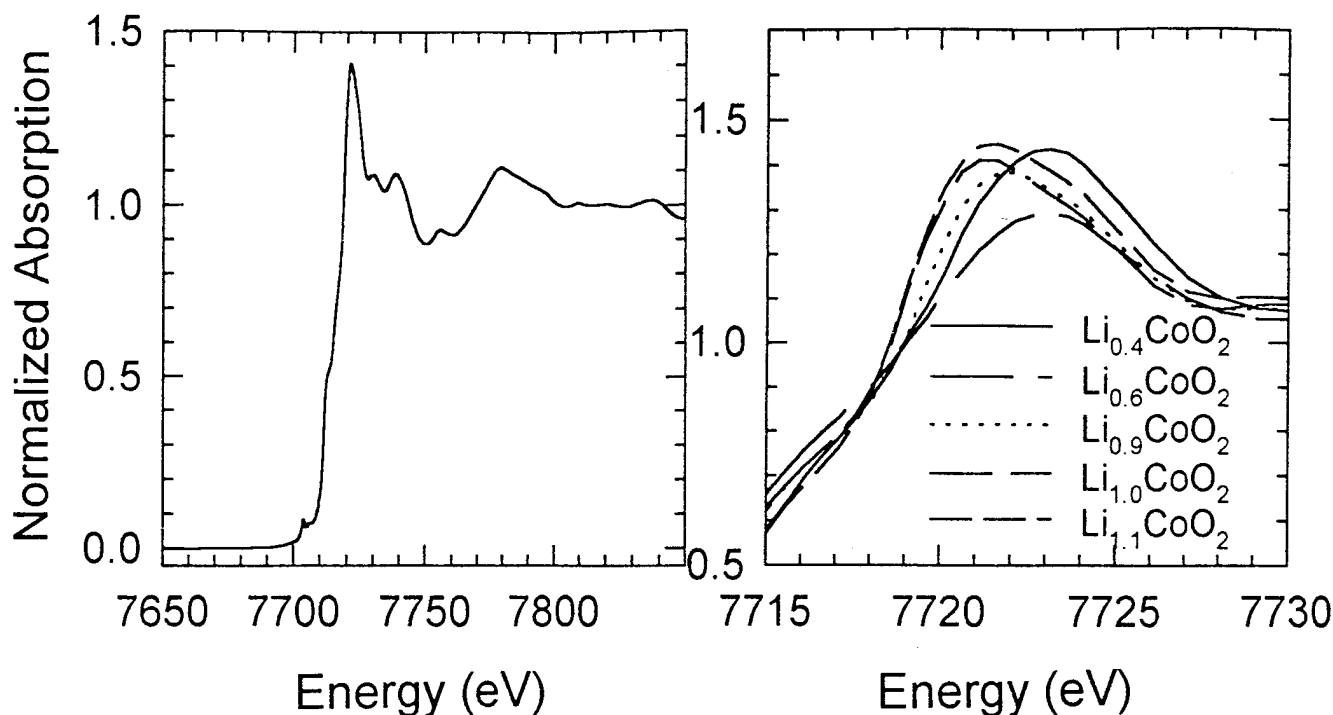


Figure 2. Cobalt K-edge NEXAFS spectra in $\text{Li}_{1-x}\text{CoO}_2$ series.

Figure 3. Detailed view of NEXAFS white line spectra for $\text{Li}_{1-x}\text{CoO}_2$ series.

coordination.⁴ The NEXAFS region also contains information, although interpretation in terms of specific electronic configurations or bonding arrangements is difficult. Nevertheless, trends observed in a series of similar materials, in this case, insertion compounds with varying amounts of Li^+ ions, can be quite useful. The x-ray absorption spectrum corresponding to the cobalt K-edge for stoichiometric LiCoO_2 is shown in Fig. 2. The overall shape of the absorption is approximately the same in all samples, but there are some subtle differences discussed below.

The main peak (or white line) absorptions are shown in Fig.3, and the peak values are listed in Table I. For the three samples with x-values 0.0 (stoichiometric), 0.1 and 0.4, the peak shifts to higher energy with decreasing Li content. This is attributed to the increase in charge on the Co ion caused by the removal of compensating electronic charge associated with the lithium deficiency. The relatively large shift (almost 2 eV over the entire range) is consistent with the expectation that the compensating electrons originate from the Co ions rather than from the generation of defect oxide species. There is no significant difference between the peak positions for the $x = 0.4$ and 0.6 materials, which may be due to the actual Li contents of the two samples being closer to each other than the nominal Li contents, and the presence of the structural phase transition in the lowest Li content sample, which can also affect the edge position.

The integrated intensity of the small pre-edge feature occurring around 7704 eV (Fig.2) is plotted in Fig.4 as a function of Li-content. The weak pre-edge absorption is attributed to the dipole-forbidden $1s \rightarrow 3d$ transition, and its intensity provides a measure of the degree of departure of the Co environment from octahedral coordination symmetry.⁵ The trend of decreasing symmetry with decreasing Li content is monotonic, even including an excess Li sample ($\text{Li}_{1.1}\text{CoO}_2$) prepared by sol-gel techniques. Departure from the trend is noted for the $\text{Li}_{0.4}\text{CoO}_2$ sample, and is, again, attributed to the structural phase transition which occurs at the lower lithium content.

Table I. NEXAFS White Line Positions

COMPOUND	NEXAFS PEAK (eV)
$\text{Li}_{0.4}\text{CoO}_2$	7722.8
$\text{Li}_{0.6}\text{CoO}_2$	7722.8
$\text{Li}_{0.9}\text{CoO}_2$	7721.6
$\text{Li}_{1.0}\text{CoO}_2$	7721.0
$\text{Li}_{1.1}\text{CoO}_2$	7721.2

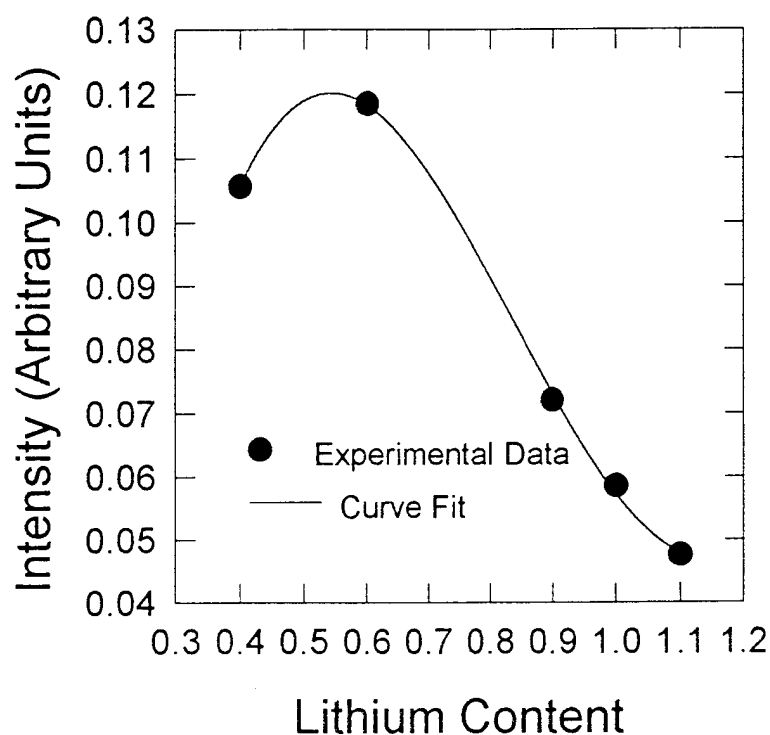


Figure 4. Plot of Co pre-edge integrated intensity vs. Li content.

The parent compound, LiCoO_2 is expected to be diamagnetic because the nominal valence of Co is 3+. It is therefore also expected that the removal of d-electrons corresponding to charge neutrality in Li-deficient samples should yield paramagnetic material. The first derivative EPR spectrum of LiCoO_2 is shown in Fig. 5a and spectra of the Li-deficient samples are displayed in Fig. 5b. The strong and relatively narrow resonance of the stoichiometric sample (5a) is attributed to the presence of the several percent Co_3O_4 impurity which was detected by x-ray diffraction. Co_3O_4 has inequivalent Co ions, two in the diamagnetic 3+ state and one in the paramagnetic 2+ state.⁶ The EPR spectra of the Li-deficient samples are, however, quite broad due to magnetic dipole-dipole interactions between spins induced by the loss of the compensating d-electrons and localized on the Co sites.

Lithium-7 NMR absorption lineshapes under static (non-spinning) conditions for $x = 0.0$, 0.1 and 0.4 are displayed in Fig. 6. The parent compound is characterized by both a small chemical shift, ~5 ppm relative to aqueous LiCl solution, and a relatively narrow line width,

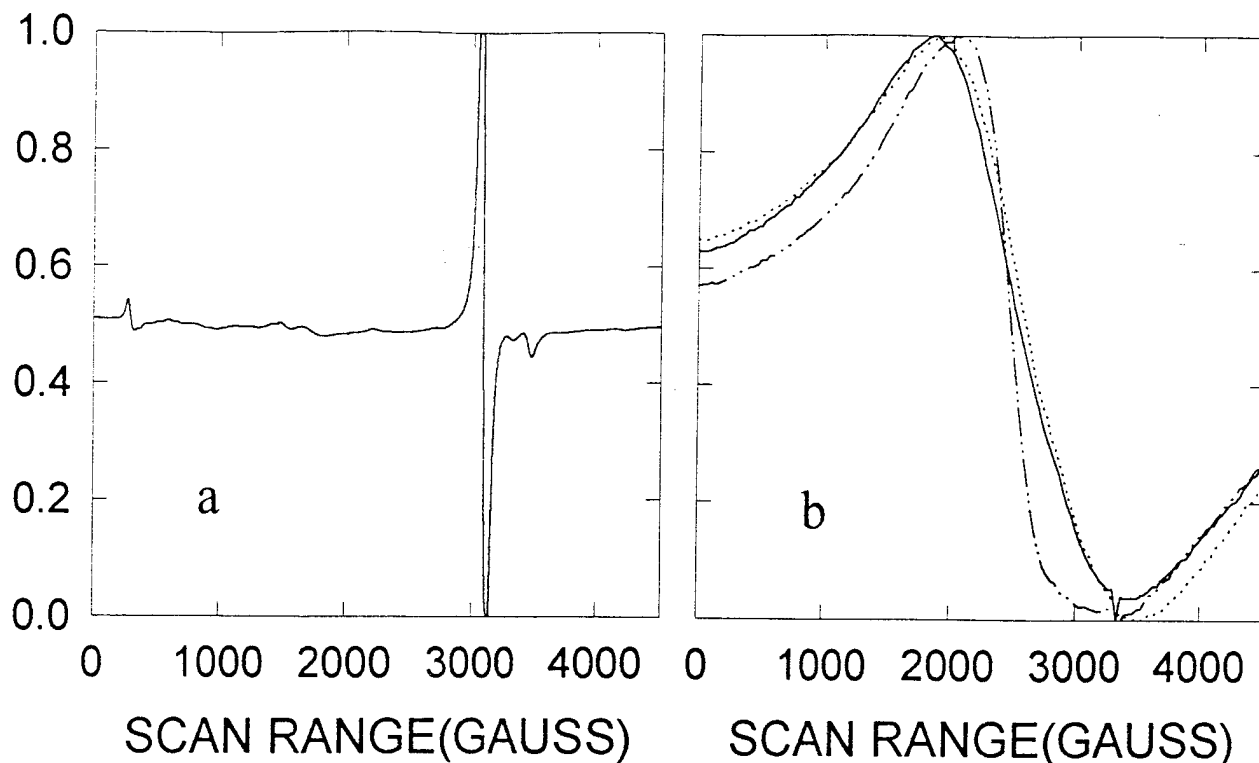


Figure 5. (a) EPR spectrum of LiCoO_2 . (b) EPR spectra of $\text{Li}_{1-x}\text{CoO}_2$; $x = 0.1$ (dots), $x = 0.4$ (solid), $x = 0.6$ (chain links). The microwave frequency is 9.42 GHz

15 kHz (130 ppm) full width at half maximum. Similar NMR results for LiCoO_2 have been reported recently.⁷ The lack of observable quadrupole satellite transitions, coupled with very low ionic mobilities inferred from variable temperature studies (to be discussed later), indicate that the Li site symmetry is high. The removal of Li results in a dramatic increase in chemical shift, values listed in Table II, as well as an increase in line width. The large chemical shifts and increased line widths of the Li-deficient materials are attributed to localized spins on the Co sites, as evidenced by the EPR results. The line widths of all four samples (including $x = 0.6$) are plotted as a function of temperature in Fig. 7. The parent ($x = 0.0$) and $x = 0.1$ compounds exhibit essentially no variation in line width over the very large temperature range between -100 to $+250^\circ\text{C}$, while the line widths of the $x = 0.4$ and 0.6 materials change by nearly a factor of two over the same temperature range.

Lithium ion mobilities in these cathode materials can be said to be fairly small compared to other intercalation cathodes such as Li_xTiS_2 , in which much more significant motional line narrowing effects are observed.⁸ Some of the line width temperature dependence of the Li-deficient materials could be attributed to motional effects, because there are more possible sites for Li^+ to occupy than in the stoichiometric compound. However, the ordinary temperature dependence of the paramagnetic susceptibility would also yield line broadening at lower temperatures. Spin-lattice relaxation (T_1) measurements were made in an attempt to distinguish between these two effects, and the results are plotted in Fig. 8. Again, the stoichiometric compound exhibits remarkably little variation over the large 350-degree range previously cited. The T_1 's of the $x = 0.4$ and 0.6 samples do change by about a factor of four over the same temperature range, but the lack of observable T_1 minima in the Li-deficient samples does not permit an estimate of motional correlation times. However, because almost no temperature variation of T_1 was noted in the more magnetic LiMn_2O_4 cathode system,⁹ some Li^+ ion motion can be deduced.

Table II. Chemical Shifts Relative to LiCl

Sample	^7Li chemical shift (ppm)
$\text{Li}_{1.0}\text{CoO}_2$	5
$\text{Li}_{0.9}\text{CoO}_2$	7
$\text{Li}_{0.6}\text{CoO}_2$	75
$\text{Li}_{0.4}\text{CoO}_2$	89

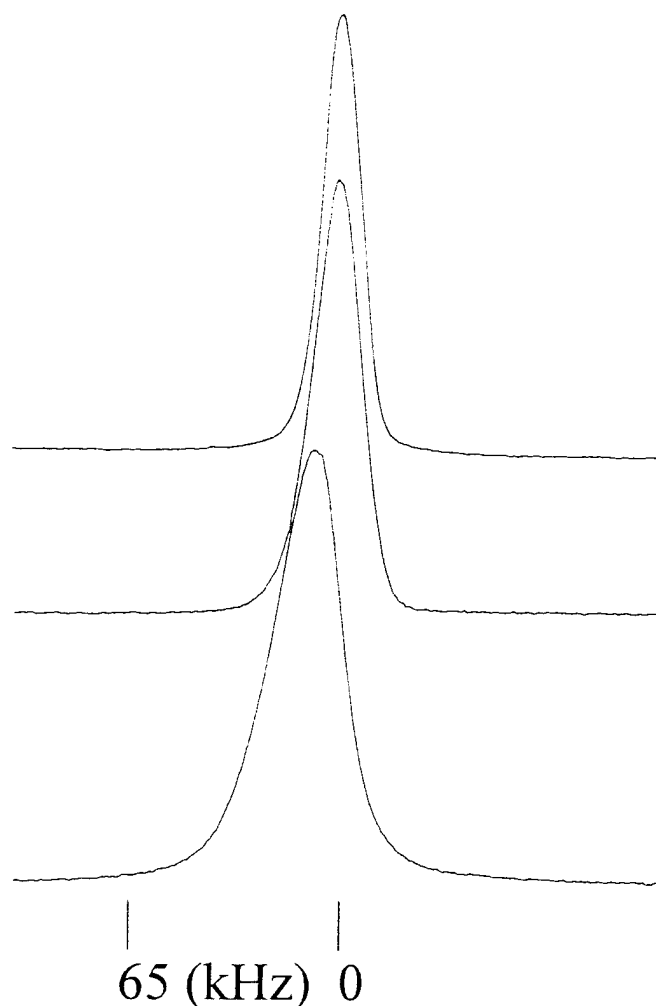


Figure 6. ^7Li NMR static spectra of $\text{Li}_{1-x}\text{CoO}_2$ arranged from top to bottom: $x = 0.0, 0.1$ and 0.4 .

Further information about the Li^+ environment in these cathode materials can be obtained by magic angle spinning (MAS) techniques. The very broad lines characteristic of the $x = 0.4$ and 0.6 samples, combined with the limited spinning rate of the current system (~ 8 kHz) made it difficult to extract structural detail for these samples. However, MAS spectra are displayed for the parent and $x = 0.1$ samples in Fig.9. While the $x = 0.0$ compound exhibits only a single narrow peak (with attendant spinning sidebands), the $x = 0.1$ sample shows two peaks: a major one in about the same position as that of the parent compound and a smaller one shifted about 6.3 kHz (~ 55 ppm) with respect to the main peak. Thus two magnetically inequivalent sites in $\text{Li}_{0.9}\text{CoO}_2$ are resolved, although most of the Li^+ ions experience an environment similar to that in the parent compound. MAS spectra for the $x = 0.4$ and 0.6 samples (not shown) do not yield evidence for distinct sites in that the "center of masses" of the lines plus sidebands are shifted and thus provide little more information than the static spectra. The shifted component in $\text{Li}_{0.9}\text{CoO}_2$ is attributed to proximity to paramagnetic cobalt ions, and the small intensity of the shifted peak relative to the main one implies that only a relatively small fraction of the cobalt ions are affected when $x = 0.1$. By the time $x = 0.4$, all of the Li ions and, by extension, all of the Co ions are affected. It certainly would have been of interest to examine intermediate-valued samples ($\text{Li}_{0.8}\text{CoO}_2$ and $\text{Li}_{0.7}\text{CoO}_2$), had they been available at the time of this investigation.

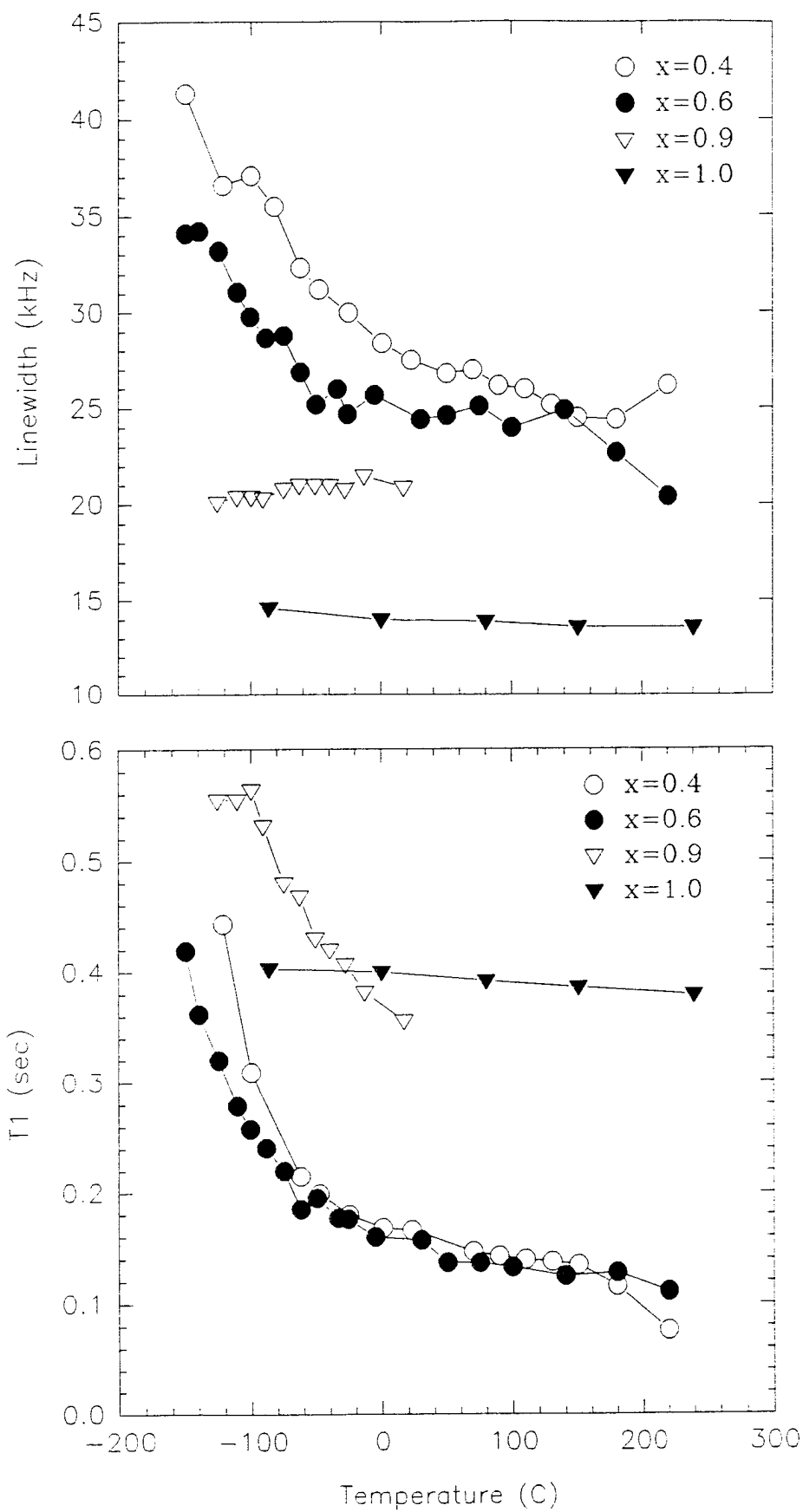


Figure 7 and 8. ^7Li NMR line widths and T_1 vs. temperature for Li_xCoO_2 series.

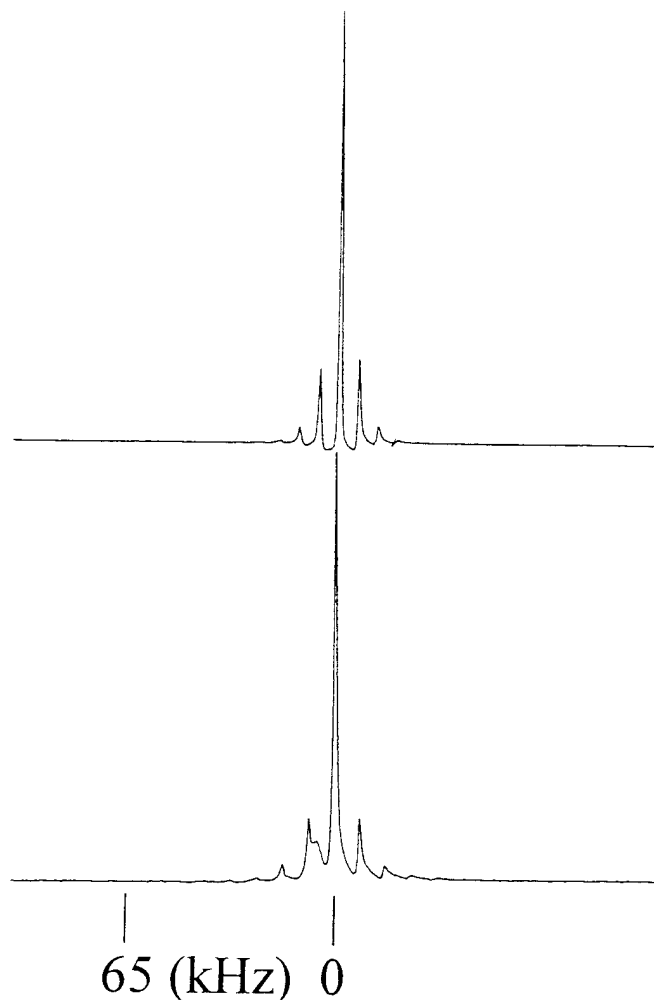


Figure 9. ^7Li NMR magic angle spinning spectra of $\text{Li}_{1-x}\text{CoO}_2$ arranged from top to bottom: $x = 0.0$, $x = 0.1$.

CONCLUSIONS

The preparation of air-stable cathodes ($\text{Li}_{1-x}\text{CoO}_2$) with variable Li content was successfully achieved in order to carry out *ex situ* spectroscopic studies. The dependence of the c-lattice parameter on x and the observation a structural phase transition (at $x \sim 0.5$) are in good agreement with the *in situ* results of Dahn and co-workers.² Cobalt K-edge NEXAFS and EPR measurements verify the expectation that compensating electrons associated with Li deintercalation originate from the Co d-orbitals. Static and MAS ^7Li NMR spectra of LiCoO_2 indicates high site symmetry for the Li^+ ions (at least tetrahedral), through lack of quadrupole splitting, and essentially complete ionization, through lack of chemical shift. Spins localized on the Co ions in Li-deficient samples result in both broadening and shifting of the ^7Li resonances. Magnetically inequivalent Li sites are resolvable in $\text{Li}_{0.9}\text{CoO}_2$, suggesting that only a relatively small fraction of the Co ions are paramagnetic in this sample.

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